

Chemistry

Lecture 2

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Hydrocarbons

Outline:

- ✚ Open chain and closed chain hydrocarbons
- ✚ Nomenclature of alkanes, alkenes and alkynes
- ✚ Benzene, properties, structure, modern representation, resonance method, Electrophilic substitution
- ✚ The molecular orbital treatment of benzene

Classification of Hydrocarbons

A) Open chain/Acyclic/Aliphatic

Saturated Hydrocarbons (Alkanes):

- Valencies of carbon atoms are fully satisfied
- They cannot take up any hydrogen atom or any other atom
- Generally give substitution reactions

Unsaturated Hydrocarbons (Alkenes):

- Valencies of carbon atoms are not fully satisfied
- They can take up any hydrogen atom or any other atom
- Generally give addition reactions

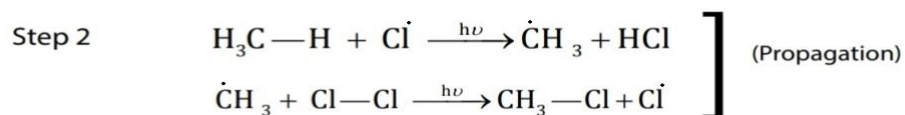
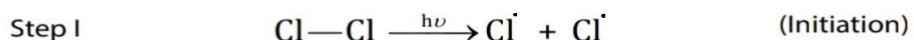
B) Closed chain/Cyclic Hydrocarbons ⇒ Alicyclic and Aromatic (Discussed in previous lect.)

Alkanes

- General formula C_nH_{2n+2}
- Paraffins
- Non polar, weak London forces
- Low M.P and B.P, increases with molecular mass or carbon chain
- sp^3 -hybridization
- Least reactive among hydrocarbons due to:
 - ☞ Non polar nature of C-H and C-C bonds
 - ☞ Inertness of σ bond
- Give free radical substitution reactions and thermal/catalytic reactions.

Halogenation

- ❖ Addition of halogen
- ❖ Free radical mechanism
- ❖ In presence of diffused sunlight
- ❖ 3 steps (initiation, propagation, termination)
- ❖ Reactivity order $F_2 > Cl_2 > Br_2 > I_2$
- ❖ F_2 reacts violently
- ❖ I_2 reacts too slowly and reaction is reversible
- ❖ R-I is not produced
- ❖ Mixture of products are obtained
- ❖ In excess of methane, CH_3Cl is major product
- ❖ In excess of Cl_2 , CCl_4 is major product



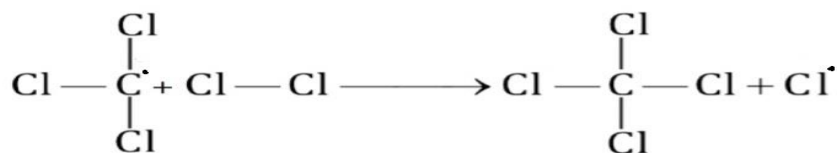
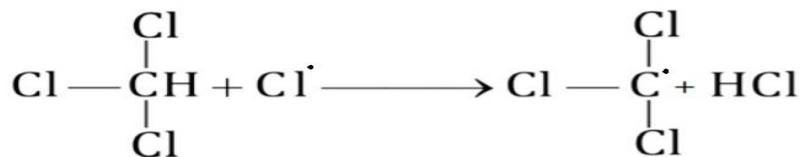
By repetition of step II, a mixture of halogen substituted products are obtained. The reaction is not synthetically so important.



Dichloromethane



Chloroform



Tetrachloromethane or
carbon tetrachloride

Alkenes

- Olefins (oil forming property)
- General formula C_nH_{2n} (for mono-enes)
- Each double bonded carbon is sp^2 hybridization
- Ethene ($CH_2=CH_2$)

The simplest alkene

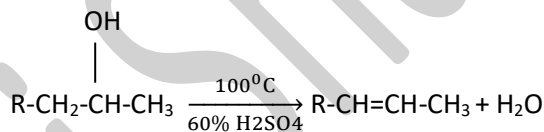
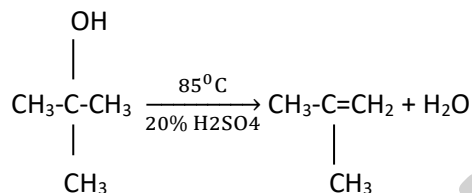
Has 5 sigma (4 with hydrogen atoms and 1 b/w both carbons) and 1 pi bond (b/w both carbons)

Has localized pi electrons

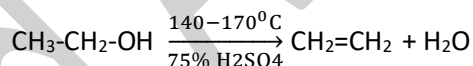
Preparation of Alkenes

(a) Dehydration of Alcohols:

3° alcohols > 2° alcohols > 1° alcohols (due to stability of carbocation, an intermediate)



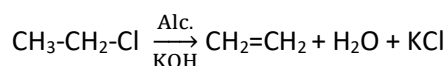
(In case of possibility of more than one kind of alkene products, choose the symmetrical alkene as product)



- What will be the product of dehydration of 2-Pentanol?
- ◆ **Dehydrating agents:** Al_2O_3 (best method), P_4O_{10} or P_2O_5 , conc. H_2SO_4 , H_3PO_4

(b) Dehydrohalogenation of Alkyl Halides:

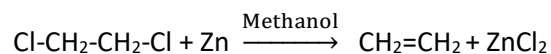
- **β** elimination reactions (E reactions)
- **β hydrogen** is removed along with halogen
- Occurs in presence of **Alcoholic KOH**
- Product is alkene
- Primary alkyl halides give E2
- Tertiary alkyl halides give E1
- Secondary alkyl halides give both E2 and E1
- If more than one **β hydrogen** are present then **β hydrogen** will be removed as so to form **symmetrical alkene**.



- What will be the product of dehydrohalogenation of 2-Chloro butane?

(c) Dehalogenation of Vicinal dihalides:

- Reaction with active metals like Mg, Zn dust (reduction) etc
- In anhydrous solvent i.e. methanol (CH_3OH) or acetic acid



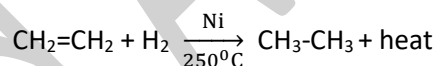
Reactions of Alkenes

- Mostly give electrophilic addition reactions
- Most reactive hydrocarbon
- Due to pi bond formed by sideways overlap (less overlap)
- Weaker than sigma bond

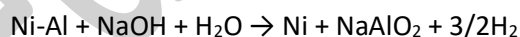
(a) Addition Reactions:

i. Hydrogenation (Reduction):

- Catalyst \gg Ni/ 250°C or Pt, Pd/room T
- Amount of heat evolved is called heat of hydrogenation
- Used in quantitative analysis
- Used in preparing vegetable ghee from vegetable oil
- Used as Synthetic as well as analytical tool



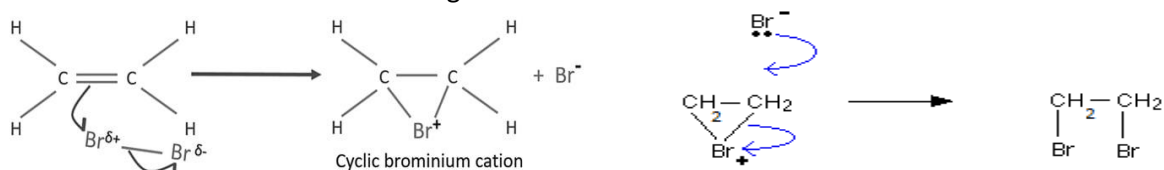
Raney Nickel



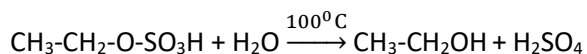
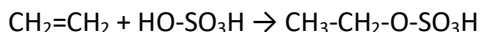
- Raney nickel has porous surface (high surface area)

ii. Halogenation:

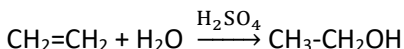
- $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$
- Bromine water test
- Unsaturation test
- Br_2/CCl_4 is added
- Brown colour of bromine discharges



iii. **Hydration:**



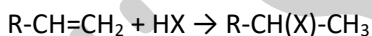
OR



- -OH group will attach with that double bonded carbon which has less no. of hydrogen atoms
- Which alkenes produce 2-Butanol?

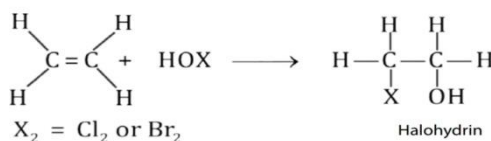
iv. **Addition of Hydrogen Halides/Halogen Acids:**

Markownikov's Rule: On addition of unsymmetrical reagent to unsymmetrical alkene/alkyne, negative part of the adding reagent goes to that double bonded carbon having less no. of hydrogen atoms and positive part to that double/triple bonded carbon having more hydrogen atoms.



- Reactivity order **HI > HBr > HCl > HF**
- Two steps involved
- Alkene molecule acts as nucleophilic centre
- Intermediate formed during mechanism acts as electrophile

v. **Addition of Hypohalous Acid:**



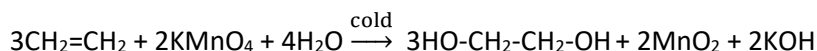
- OH is negative end and X is positive end of hypohalous acid

(b) **Oxidation Reactions:**

i. **Hydroxylation:**

◆ **Dil. Cold KMnO₄**

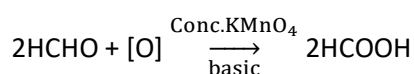
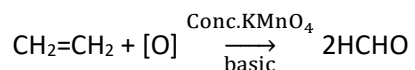
- Unsaturation test
- Baeyer's reagent (cold 1% alkaline KMnO₄ solution)
- Pink colour of KMnO₄ discharges
- Products are stable vicinal glycols (simply glycols)
- These glycol can be oxidized to aldehydes and carboxylic acids by using strong oxidizing agents (conditional)



- The product ethylene glycol is stable under these conditions
- In presence of strong oxidizing agent, ethylene glycol will oxidize to form glyoxal which will further oxidize to oxalic acid

◆ **Conc. Hot KMnO₄**

- Produces two molecules of carboxylic acid (final product if aldehyde was initially produced)
- Formic acid further oxidizes to CO₂
- It is oxidative cleavage
- Unsaturation test as well as for the location of double bond
- Double bonded carbon will convert into carbonyl group

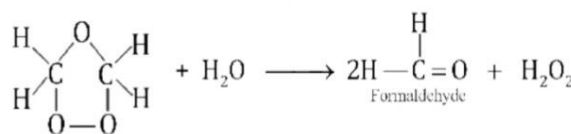
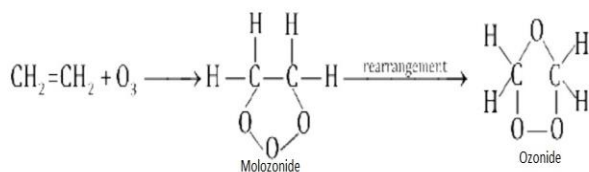


- Which alkene produces 1 mole of acetic acid and 1 mole of propanoic acid?

ii. **Ozonolysis:**

- A test for location of double bond
- Ozone is allotropic form of oxygen
- Products are aldehydes/ketones

Ozonides are unstable compounds and are reduced directly by treatment with zinc and H₂O. The reduction produces carbonyl compounds (aldehydes or ketones).

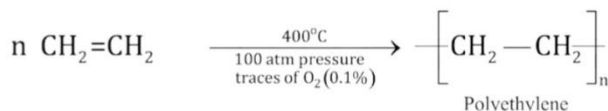


- 2-Butene will produce?

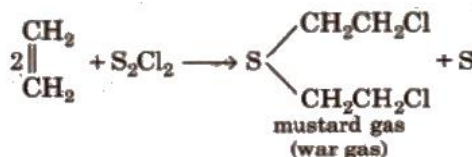


(c) **Polymerization:**

- Small molecules combine to form large molecule
- C-C bond length is high in polymer than in monomer
- Mixture of Al(C₂H₅)₃ and TiCl₄ is used for good quality
- Optimum conditions; **T=400°C, P=100 atm, 0.1% O₂, Catalyst [TiCl₄ + Al(C₂H₅)₃]**



Mustard Gas:



- High boiling liquid
- Highly vesicant
- Causes blisters

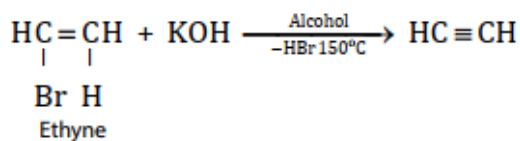
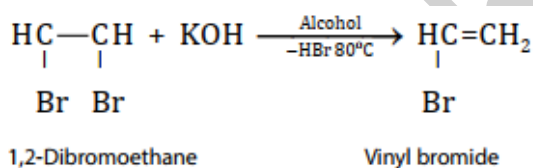
Alkynes

- General formula C_nH_{2n-2} (for mono-ynes)
- Each triple bonded carbon is sp hybridization
- Ethyne ($CH\equiv CH$), the simplest alkyne

Preparation of Alkynes

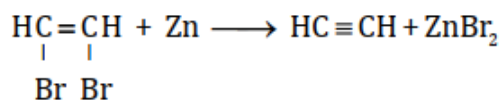
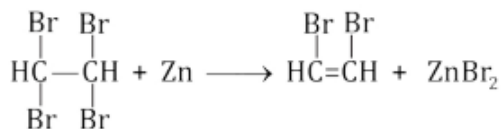
(a) Dehydrohalogenation of Vicinal dihalides:

- β elimination reactions (E reactions)
- β hydrogen is removed along with halogen
- Occurs in presence of **Alcoholic KOH**
- Elimination occurs from adjacent carbons twice



(b) Dehalogenation of Vicinal tetrahalides:

- Reaction with active metals like Mg, Zn dust (reduction) etc
- In anhydrous solvent i.e. methanol (CH_3OH) or acetic acid

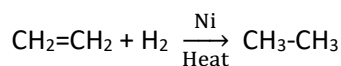
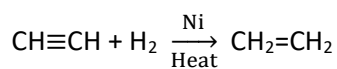


Reactions of Alkynes

- Mostly give electrophilic addition reactions
- Less reactive than alkene towards electrophilic addition reaction due to presence of triple bond which reduces bond length making it difficult to break
- More reactive than alkene towards nucleophilic reagents

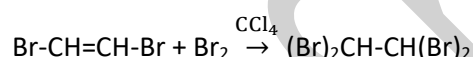
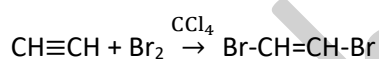
(a) Addition Reactions:

i. Hydrogenation (Reduction):



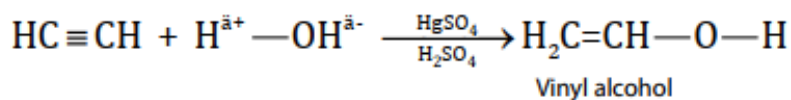
ii. Halogenation (addition of X₂):

- F₂ > Cl₂ > Br₂ > I₂
- Bromine water (Br₂/CCl₄) test (unsaturation test)
- Brown colour of bromine discharges

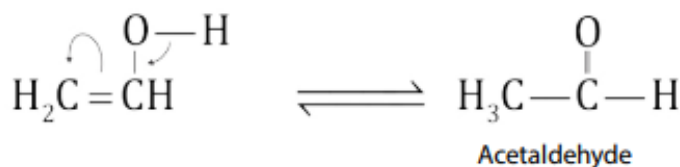


iii. Hydration (addition of H₂O):

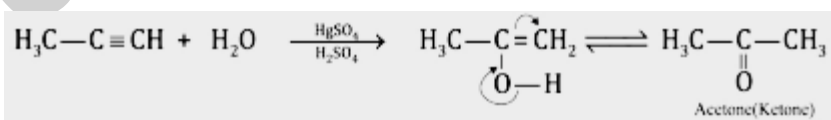
Water adds to alkynes in the presence of mercuric sulphate dissolved in sulphuric acid at 75°C. The reaction is important industrially. For example,



Vinyl alcohol is an unstable enol. The enol has the hydroxy group attached to a doubly bonded carbon atom and isomerises to acetaldehyde.



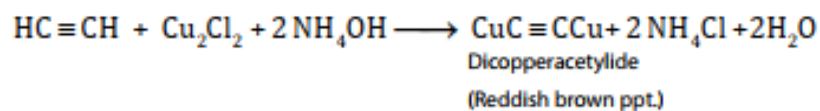
All other alkynes give ketones.



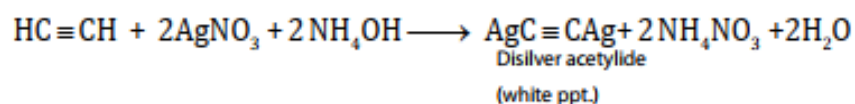
- Double bonded carbon to which –OH will be attached in enol form will become carbonyl group after rearranging.
- Butanone is produced from which alkyne?
- 2-pentyne producesketone?

Acidity of Alkynes

- ❖ Ethyne and terminal alkynes (1-alkynes) like propyne, 1-butyne, 1-pentyne show acidic nature
- ❖ Hydrogen is bonded to sp-hybridized carbon through sp-s overlap
- ❖ sp-hybridization makes carbon more electronegative
- ❖ sp-hybridized carbon pulls electrons towards itself making hydrogen atom acidic
- ❖ 1-Alkynes or ethyne form alkynides or acetylides [both ionic in nature] with molten Na and sodamide (NaNH_2)
- ❖ **Ammoniacal solution of cuprous chloride**



- ❖ **Ammoniacal solution of silver nitrate**



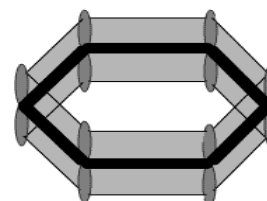
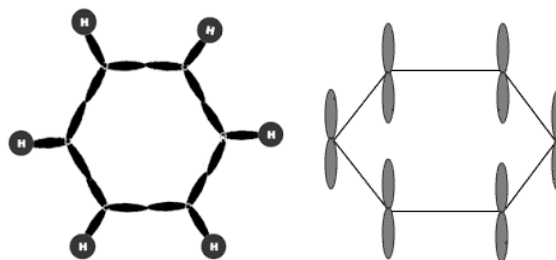
- ❖ Acetylides react with mineral acids i.e. HCl , HNO_3 , H_2SO_4 etc to recover acetylene
- ❖ These alkynides are used for the preparation, purification, separation, and identification of alkynes.

Benzene

- Discovered by Michael Faraday by destructive distillation of vegetable oil.
- Found in coal-tar by Hoffmann.
- Benzene is a colorless liquid with particular smell and taste
- It is flammable

Structure:

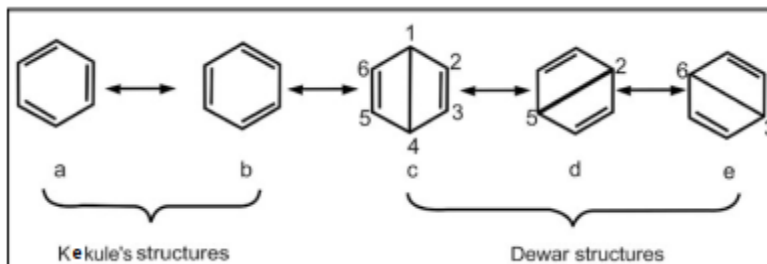
- Stability is explained on basis of;
 - ☞ Resonance method (resonance energy of benzene = + 150.5 kJmol^{-1})
 - ☞ **Atomic orbital treatment**
- Each carbon is sp^2 hybridized
- Hexagonal planar
- 120° bond angle
- Delocalized pi electrons
- Stable molecule
- Continuous sheath of electronic cloud formed
- Sandwich structure obtained
- Strong electrophile is prepared
- Reluctant to electrophilic addition reactions
- Prefer electrophilic substitution reactions
- Don't give elimination and polymerization reaction



Continuous sheath of es-1

Resonance method

- The possibility of different pairing scheme of valence electrons of atoms is called resonance and the structures thus obtained are resonance structures.



- Resonance hybrid structure is represented with circle (solid or dotted) inside the ring

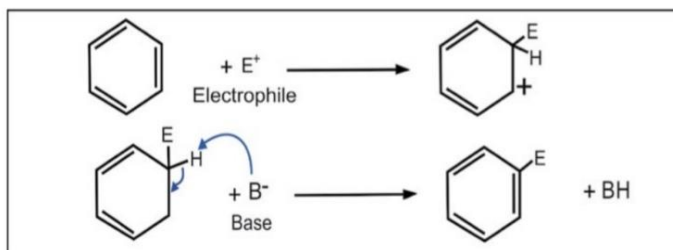


In alkanes the C-C bond length is 1.54Å.
In alkenes the C = C bond length is 1.34Å.
In alkynes the C \equiv C bond length is 1.20Å.
In benzene the C-C bond length is 1.397Å.

Electrophilic Substitution Reactions

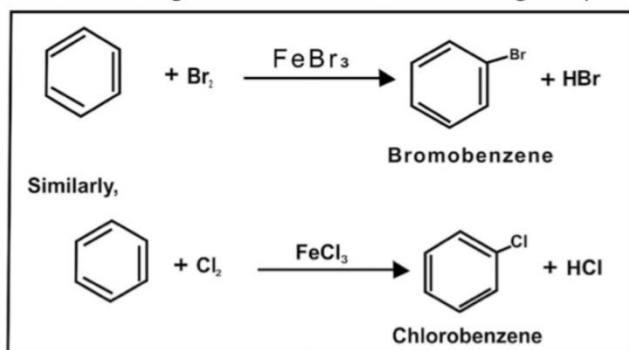
- These reactions prove benzene is very stable molecule
- Strong electrophile is required to break stable pi electronic cloud of benzene

General Mechanism:



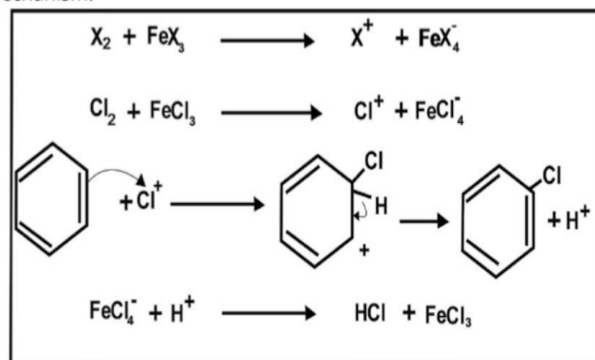
1. Halogenation

The introduction of halogen group in benzene ring is called "Halogenation". Benzene reacts with halogen in the presence of a catalyst like FeBr_3 , AlCl_3 , etc. Chlorination and bromination are normal reactions but fluorination is too vigorous to control. Iodination gives poor yield.



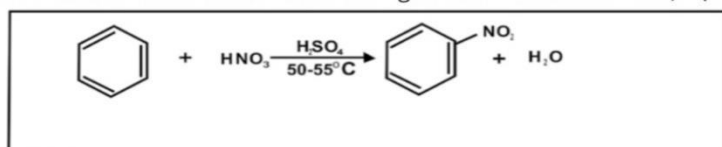
Mechanism:

The actual halogenating agent is X^+ (i.e. Cl^+ or Br^+) is formed by the following mechanism.

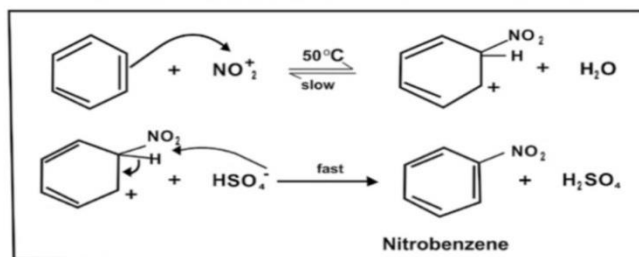


2. Nitration

The introduction of NO_2 group in benzene ring is called "Nitration". The nitration of benzene takes place when it is heated with a 1:1 mixture of con. HNO_3 and con. H_2SO_4 at 50-55°C. Sulphuric acid reacts with nitric acid to generate nitronium ion, (NO_2^+).



Mechanism:

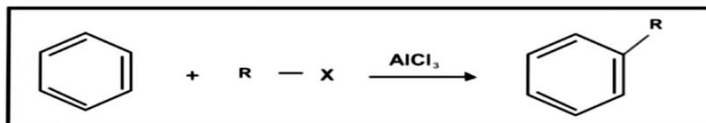


4. Friedel-Crafts Reactions

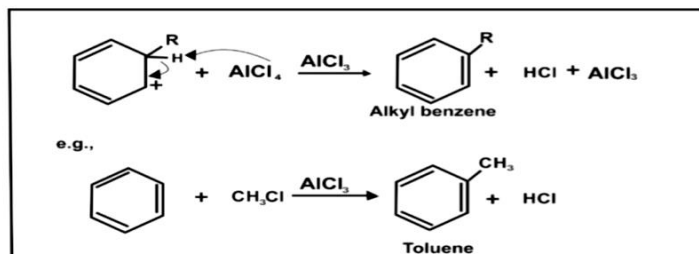
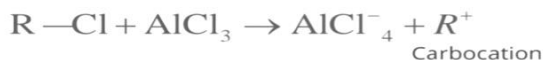
The alkylation and acylation of benzene are called Friedel-Crafts reactions.

a) Alkylation

The introduction of an alkyl group in the benzene ring in the presence of an alkyl halide and a catalyst AlCl_3 is called Friedel-Crafts alkylation or Alkylation.

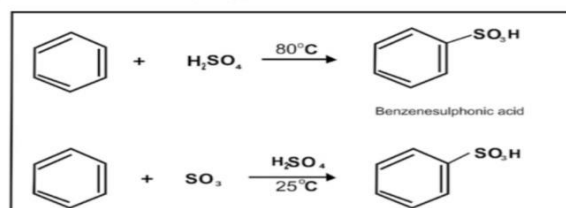


Mechanism:



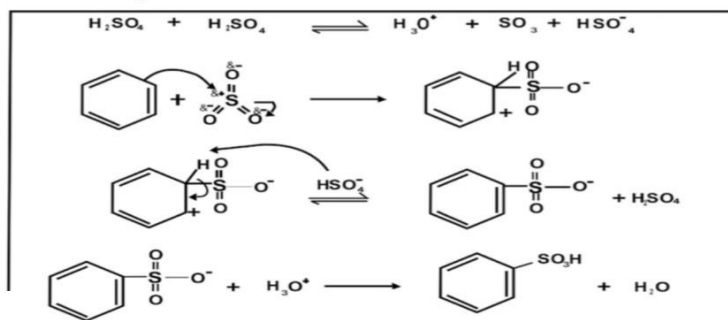
3. Sulphonation

The introduction of sulphonic acid group in benzene ring is called Sulphonation. When benzene is heated with fuming H_2SO_4 or conc. H_2SO_4 it yields benzene sulphonic acid.



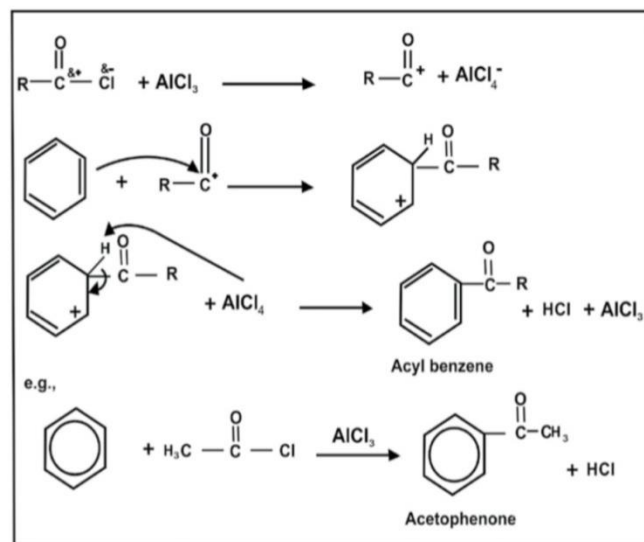
Mechanism:

When sulphuric acid alone is used, the actual electrophile in this reaction is SO_3 .



b) Acylation:

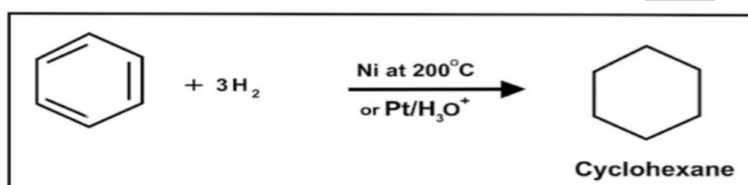
The introduction of an acyl group R-C(=O)- in the benzene ring in the presence of an acyl halide and a catalyst AlCl_3 is called Friedel Crafts Acylation or Acylation.



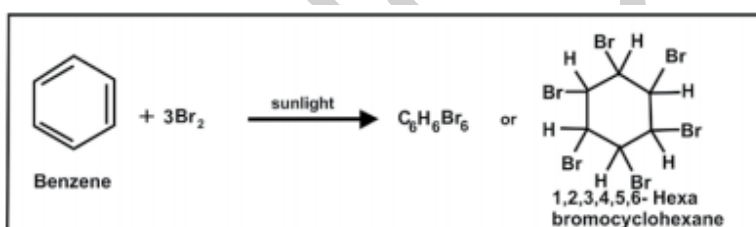
- Positive electrophiles in Electrophilic substitution reactions are called asonium ions i.e. Cl^+ chloronium ion, NO_2^+ nitronium ion, R^+ alkylonium ion, CH_3^+ methylonium ion, RCO^+ acylonium ion, CH_3CO^+ acetylonium ion etc.
- Introduction of CH_3^+ in benzene ring is called Methylation
- Introduction of HCO^+ is called Formylation and CH_3CO^+ Acetylation
- In all Electrophilic substitution reactions **hybridization changes from sp^2 (planner) in benzene to sp^3 (tetrahedral) in intermediate and finally to sp^2 (planner) in product.**

Addition Reactions

Hydrogenation of Benzene



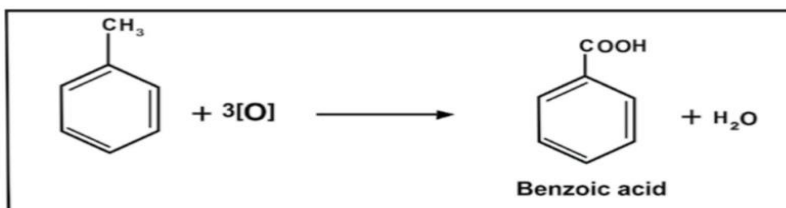
Halogenation of Benzene



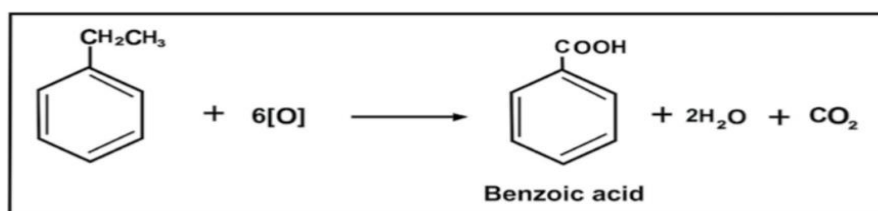
Side chain Reactions

Side chain Oxidation of Benzene (alkyl benzene)

- Strong oxidizing agent ($\text{KMnO}_4/\text{H}_2\text{SO}_4$) is used
- Pink colour of KMnO_4 discharges
- Distinguish alkyl benzenes from other substituted benzenes

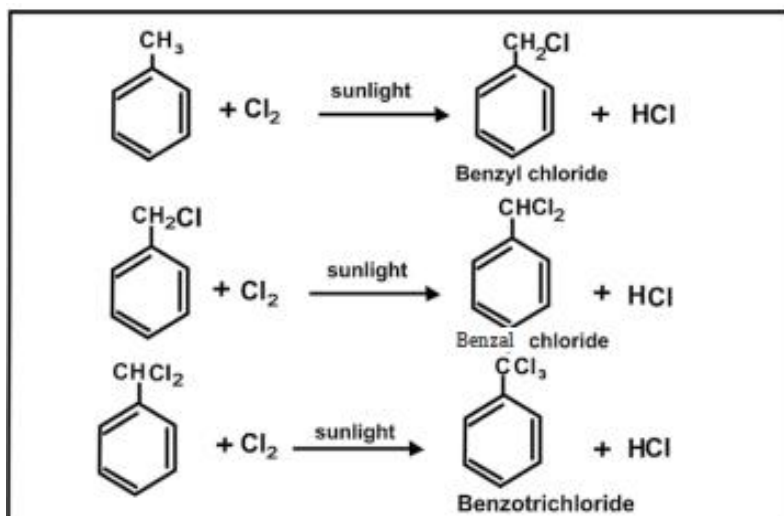


Whatever the length of an alkyl group may be it gives only one carboxyl group. Moreover the colour of KMnO_4 is discharged. Therefore this reaction is used as a test for alkybenzenes.



- Benzoic acid is the product

Side chain Halogenation of Benzene (Methyl benzene)



Substitution on Benzene Ring by 2,4- directing or 3,5- directing Groups

2,4 (Ortho-para directing groups)	3,5 (meta directing groups)
Electron donating	Electron withdrawing
Release electron on benzene ring	Withdraw electron from benzene ring
Increase availability of electrons on 2,4 positions	Decrease availability of electrons on 2,4 positions
Direct the attack of electrophile at 2, 4 positions	Direct the attack of electrophile at 3, 5 positions
Activate the ring (except halogens) Increase nucleophilicity of benzene	Deactivate the ring (decrease nucleophilicity of benzene)
Ex.: $-\text{CH}_3$, $-\text{NH}_2$, $-\text{NHR}$, $-\text{SH}$, $-\text{OCOR}$, $-\text{OH}$, $-\text{OCH}_3$, $-\text{N}(\text{CH}_3)_2$, $-\text{Cl}$, $-\text{Br}$, $-\text{I}$	Ex.: $-\text{NO}_2$, $-\text{NR}_3^+$, $-\text{CN}$, $-\text{COOH}$, $-\text{CHO}$, $-\text{COR}$, CCl_3